MESITYL KETONES AND THE ORTHO EFFECT

BY

CHARLES HARLAN McKEEVER

B.S., Illinois Wesleyan University, 1936

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS,
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INTRODUCTION

Mesityl ketones are peculiarly well adapted to the study of the *ortho* effect. Not only are they readily available but they tend to undergo types of reactions in which steric influences are particularly pronounced. The present study has as its original purpose the investigation of the influence of the mesityl radical on the formaldol condensation, that is, the condensation of mesityl ketones with formaldehyde.

Findings in this connection, however, opened up a much larger field than that originally contemplated, and some studies were directed toward exploration of the new possibilities. In this way three additional projects grew up around the original objective. Accordingly, the work falls naturally into four closely related studies. Because of this the present report has been separated into four parts—the action of paraformaldehyde or mesityl ketones (Part A), the chloromethylation of aryl ketones (Part B), a synthesis and study of vinyl mesityl ketone (Part C), and an enediol from hexaethylbenzil (Part D).

DISCUSSION AND EXPERIMENTAL

Part A

The condensation of paraformaldehyde with acetomesitylene in the presence of methanol and anhydrous potassium carbonate has been shown to yield the unsaturated ether, $C_9H_{11}COCCH_2OCH_3$, with CH_2 as a double bond, and a dimolecular product having the structure

$$C_9H_{11}COCCH{=}CCOC_9H_{11}.$$
$$\quad\quad\quad

Part B

A method has been discovered for the nuclear chloromethylation of aromatic ketones. It consists in treating the ketone with paraformaldehyde in the presence of an excess of concentrated hydrochloric acid and is somewhat similar to the procedure developed by Blanc [1] for aromatic hydrocarbons and extended by others, notably Quelet [2] to other types of compounds. The method has been applied successfully to 2,4-dimethylacetophenone, acetomesitylene, acetoisodurene, propiomesitylene, isobutyromesitylene, pivalylmesitylene, benzoylmesitylene and 2,4,6-triethylacetophenone. The yields varied from 25 to 88 per cent of the theoretical, the average yield being 60 per cent.

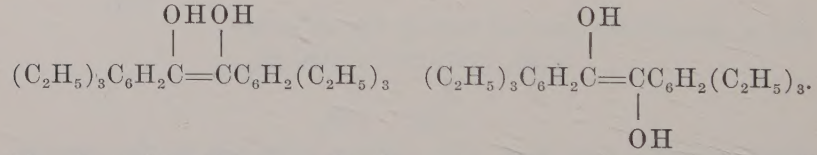
Part C

Vinyl mesityl ketone has been synthesized from β-chloropropionyl chloride and mesitylene by the Friedel-Crafts method. Catalytic reduction produced propiomesitylene and treatment with bromine gave α,β-dibromopropiomesitylene.

Vinyl mesityl ketone shows no tendency to polymerize spontaneously or in the presence of peroxides. However, polycondensation was induced by heating with methanol and anhydrous potassium carbonate. The chief product is a trimer which has been shown to be 1,3,5-trimesitoylcyclohexane. The structure of the trimer has been proved by an independent synthesis.

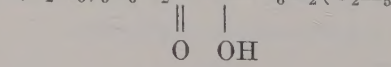
Part D

Two isomeric enediols have been prepared by the hydrogenation of hexaethylbenzil.[3] They have been assigned the *cis* and *trans* configurations



The *cis* modification may also be prepared by treatment of 2,4,6-triethylbenzoyl chloride with the binary mixture, $Mg + MgI_2$.[4]

The two enediols have been characterized and transformed into a number of derivatives including the benzoin



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[2] Quelet and Allard, Compt. rend., 205, 238 (1937).

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VITA

The writer was born near Gibson City, Illinois, June 6, 1912. He attended the public schools of Ford County and was graduated from Drummer Township High School in June, 1929. He entered Illinois Wesleyan University in the fall of 1932 and in June, 1936, received a Bachelor of Science degree. In September, 1936, he enrolled in the University of Illinois where he held a teaching assistantship from 1936 to 1938 and a Röhm and Haas research assistantship from 1938 to 1940.